Electronic Supplementary Information Novel Agaric-Derived Olive-like Yolk-shell Structured

MnO@C Composites for Superior Lithium Storage

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1. Experimental

1.1. Materials synthesis

The materials were prepared by first mixing the dried agaric (6.0 g, Dongning Beiyu Liangren Shanzhen Food Co., Ltd., China, Fig. S1) with deionized water (100 mL) in a 120 mL Teflon-lined autoclave at 120 °C for 12 h. The mixture was then ultrasound for 30 min to form a brown agaric-based colloidal solution. Next, KMnO₄ (0.79 g, 0.5 mmol, Xilong Chemical Co., Ltd, China) was added to the as-obtained brown agaric-based colloidal solution (100 mL) under continuous stirring for 30 min to form a homogeneous Mn-agaric biomass hydrogel (Fig. S2) at 180 °C for 18 h in a 120 mL Teflon-lined autoclave. The resultant hierarchical olive-like core-shell MnCO₃@C (MnCO₃@C-OCS) precursor was collected by filtration and dried overnight at 60°C. Subsequently, MnCO₃@C-OCS was annealed at 800 °C for 2 h (5 °C/min) under N₂ atmosphere to yield hierarchical olive-like core-shell MnO@C (MnO@C-OCS). Finally, the black MnO@C-OCS powder was etched by hydrochloric acid solution (1 M) to obtain hierarchical olive-like yolk-shell MnO@C composite, denoted as MnO@C-OYS.

2. Material characterization

The detailed morphologies of the samples were investigated by scanning electron microscopy (SEM, FEI Quanta200F) and transmission electron microscopy (TEM,

Tecnai G2 F20). X-ray diffraction (XRD, Bruker D8 Focus), Raman spectrometry and X-ray photoelectron spectroscopy (XPS) were used for structural and composition characterization of the products. Thermogravimetric analysis (TGA) was utilized to determine the content of the active materials. Brunauer-Emmett-Teller (BET) analyses were performed on a JW-BK132F instrument.

3. Electrochemical measurements

The electrochemical properties of MnO@C samples were studied in 2025 cointype cells with Li foil as the counter electrode, polypropylene membrane as the separator, and 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (volume ratio, 1:1) as the electrolyte. The working electrodes were prepared by spreading a homogeneous slurry composed of MnO@C samples (80%), Super P (10%), and PVDF (10%) (mass ratio) dispersed in N-methylpyrrolidone (NMP) onto Cu foil followed by drying overnight at 60 °C. The loading density of MnO@C composite was set to 0.8–1.0 mg cm⁻². The cyclic voltammetry (CV) experiments at different scan rates were carried out on CHI660D at potentials of 0.01–3.0 V. The electrochemical impedance spectroscopy (EIS) studies were recorded on a Princeton PARSTAT 4000 machine at frequencies between 100 kHz and 0.01 Hz. The galvanostatic charge/discharge measurements were obtained on Neware-BTS3000 battery testing system.

Supplementary Figures and Tables



Fig. S1 The photograph of black used dried agaric.



Fig. S2 The photograph of actual state of the Mn-agaric biomass hydrogel.



Fig. S3 SEM images of (a) MnCO₃@C-OCS composite, (b) MnO@C-OCS composite and (c) MnO@C-OYS composite.



Fig. S4 TEM image of the hollow olive-like carbon shell.



Fig. S5 XRD patterns of intermediate materials.



Fig. S6 Raman pattern of the MnO@C-OYS composite.



Fig. S7 Nitrogen adsorption-desorption isotherms and corresponding pore size distribution curve (inset) of (a) MnO@C-OYS composite, (b) MnO@C-OCS composite.



Fig. S8 TGA curve of (a) MnO@C-OYS composite, (b) MnO@C-OCS composite. The MnO content in the samples was calculated based on the following formula.





Fig. S9 XRD pattern of the MnO@C-OYS composite after annealing at 350°C in air.



Fig. S10 XPS spectra of MnO@C-OYS composite. (a) Survey spectrum, high-resolution of (b) Mn 2p, (c) O 1s, and (d) N 1s.

The Mn 2p spectrum in Fig. S10b can be fitted by two signals: Mn $2p_{3/2}$ (641.7 eV) and Mn $2p_{1/2}$ (653.5 eV) that matched-well the MnO characteristics.^{1,2} Mn-O

(530.1 eV), C-O (531.3 eV), and C=O (532.8 eV) peaks existed in O 1s spectrum (Fig. S10c).^{3,4} Besides, N 1s spectrum in Fig.S10d was resolved into three doping forms of pyridine-N, pyrrolic-N and graphitic-N recorded at 398.4 eV, 398.4 eV and 401.4 eV, respectively.⁵



Fig. S11. (a) Nyquist plots of the MnO@C-OYS and MnO@C-OCS electrodes before cycling. (b) The relationship between Z' and the reciprocal square root of the angular frequency in low frequency.

The lithium ions diffusion (D_{Li^+}) coefficients of both electrodes can be obtained by Eqs. (1) and (2):^{6,7}

$$Z' = Rs + Rf + Rct + \sigma_W \omega^{-1/2} \tag{1}$$

$$D_{Li+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma_w^2}$$
(2)

where *A* stands for the electrode area, *n* is the number of electrons, *F* denotes the Faraday constant, *C* is the molar concentration of Li⁺, *R* is the gas constant, *T* represents the absolute temperature, and σ is the Warburg coefficient. The σ_W can be calculated from the linear fitting of Z' versus $\omega^{-1/2}$ (Fig. S11b). The kinetic parameters of the MnO@C-OYS electrode are shown in Table S2.



Fig. 12 (a) Nyquist plots of the MnO@C-OYS electrode after 100 cycles. (b) The relationship between Z' and the reciprocal square root of the angular frequency in low frequency.



Fig. S13 The capacitive contributions of the MnO@C-OYS electrode at 0.8 mV s⁻¹.

According to the reported in previous manuscripts, the specific capacitive effect can be analyzed by the relationship between peak current (*i*) and scan rate (*v*) according to Eqs. (3) and (4):^{8,9}

$$i = a v^b \tag{3}$$

$$log (i) = b log (v) + log (a)$$
(4)

where a and b are constant. *b* values close to 0.5 reflect diffusion-controlled process, while values close to 1.0 refer to surface capacitive behavior.

Moreover, the contribution ratios of two different processes can further be evaluated by Eqs. (5) and (6):^{8,9}

$$i = k_1 v + k_2 v^{1/2}$$
^{S8}
(5)

$$i/v^{1/2} = k_1 v^{1/2} + k_2 \tag{6}$$

where k_1v is the contribution from the surface capacitive behavior and $k_2v^{1/2}$ represents the contribution from the diffusion-controlled process.



Fig. S14 SEM image of the MnO@C-OYS electrode after 400 cycles at 0.5 A g⁻¹.

Sample	Current density (A g ⁻¹)	Cycle number	Capacity (mAh g ⁻¹)	Ref.
MnO/C nanorods	0.5	500	667	10
MnO/biocarbon	0.5	1000	783	11
MnO@NC composites	0.5	200	784	12
MnO/C nanopeapods	2.0	1000	525	13
Pomegranate-like MnO@C microspheres	2.0	2000	527	14
N-doped MnOnanoparticles	0.1	350	754	15
MnO@NC nanocapsules	0.5	500	767	16
MnO@NPC nanotubes	0.25	250	512	17
MnO@C-OCS	0.5	400	412.5	This work
MnO@C-OYS	0.5	400	945.1	This work
MnO@C-OYS	5	1000	238.5	This work

Tables S1. Electrochemical performance comparison of some MnO/C composites reported anode materials for LIBs.

Tables S2. Kinetic parameters of the MnO@C-OYS electrode.

Sa	mple	R _s	R _{ct}	Wo	$CPE_i(F)$	σ	D_{Li^+}

	(Ω)	(Ω)	(Ω)	Q-Y ₀	Q-n		(cm^2s^{-1})
MnO@C-OYS (before cycling)	1.50	144.50	145.12	2.43x10 ⁻⁵	0.73	241.87	1.49x10 ⁻¹³
MnO@C-OCS (before cycling)	1.31	191.60	165.50	2.57x10 ⁻⁵	0.71	333.16	7.99x10 ⁻¹⁴
MnO@C-OYS (100 th)	1.28	109.70	86.50	6.21x10 ⁻⁵	0.66	48.58	3.71x10 ⁻¹²

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